

meteorologists to form a more definite idea of the prospects of approaching seasons.

We wish to express our thanks to Dr. W. N. Shaw, F.R.S., who has kindly assisted the work by permitting us to utilise the valuable collection of pressure data deposited in the archives of the Meteorological Office.

We also owe a debt of gratitude to Messrs. W. Moss and T. F. Connolly, who have shown great zeal in completing the necessary computations and drawing the numerous curves which were required for the different stations that have been investigated.

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“The Spectrum of the Radium Emanation.” By Sir WILLIAM RAMSAY, K.C.B., F.R.S., and Professor J. NORMAN COLLIE, F.R.S. Received May 18,—Read May 19, 1904.

Attempts have been made since July, 1903, to see and map the spectrum of the emanation from radium, for at that date the conversion of the emanation into helium was observed by Ramsay and Soddy, and during the first discharge of the induction current through the emanation, it was believed that a peculiar spectrum was noticed; indeed, three lines were persistent, and were mentioned in the communication on the subject in these ‘Proceedings.’

But such attempts have uniformly failed; at the first moment of the discharge, indeed, a brilliant spectrum has twice been observed, which soon became confused and indistinct. It faded before it was possible to map it, and owing to the presence of impurities, generally carbon monoxide, nitrogen, or hydrogen, the special spectrum was obscured. All that could be said was that it appeared to present some brilliantly green lines.

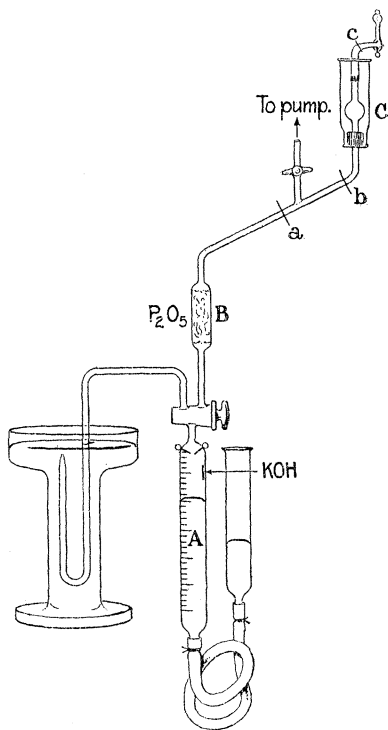
These experiments, however, have not been fruitless; they have led to better knowledge of the precautions which it is necessary to take to eliminate impurities. The arrangement of the apparatus, too, has been simplified, and the manipulation made easier. As it is possible that others may wish to repeat the experiments, and may perhaps have even better success in mapping the spectrum, we think it well to enter into the details of the manipulation somewhat minutely, and to give a woodcut of the apparatus employed.

The stock of radium bromide (about 109 milligrammes) dissolved in about 10 c.c. of water in two small bulbs was attached by sealing to a small Töpler’s pump. Between the pump and the bulb there was a stop-cock, greased, of course, to insure freedom from leakage; but in order to prevent the long contact of the emanation with the stop-cock, and its possible contamination with carbon dioxide, the mercury from

the pump was caused to flow past the stop-cock by raising the reservoir of the pump and closing the exit tube at its lower end; the mercury slowly leaked past the valve of the pump, passed the tap (which was then shut), and so confined the space above the radium bromide by means of mercury. As radium bromide yields electrolytic gas, containing an excess of hydrogen, the pressure gradually rose; the mercury in contact with this gas remained perfectly bright, and showed no tendency to adhere to the glass; the presence of ozone thus appears to be excluded, but this excess of hydrogen will form the subject of a future communication.

The emanation was allowed to accumulate for 14 days. The pump was exhausted until no trace of a bubble passed down the capillary exit tube. But as even then a trace of air must have remained in the barrel, the tap leading to the bulbs containing the radium bromide was turned rapidly, so as to admit a trace of the electrolytic gas into the pump and "wash it out." This gas was rejected. The remaining electrolytic gas with the emanation was collected in a tube which had previously been heated to redness, and then twice washed out with pure oxygen. The mercury in the collecting tube was then boiled, and the bubble of gas removed. It was hoped thereby to have eliminated every trace of nitrogen. The gas was then introduced into the gas-burette, shown in the figure, through the inverted syphon. All the mercury was freshly filtered and pure. The apparatus, too, was freshly constructed and heated to redness to burn out traces of dust. The gas-burette had been washed out with alkali and with nitric acid, and then with a stream of distilled water; it was dried by drawing through it a stream of dust-free air. Some slightly moist caustic potash was melted on to the glass, near the sparking wires; this was intended to absorb any trace of carbon dioxide which might have chanced to be formed during the explosion of the electrolytic gas by the burning of dust. The rubber tube was cemented

FIG. 1.



on to the burette; the burette was washed out twice with oxygen, and by lowering the reservoir several times the upper end was made a torricellian vacuum; it was left thus for some time, so as to insure the removal of adhering nitrogen from the walls of the tube.

The electrolytic gas was then introduced, and exploded. As the explosion-burette was graduated, the total volume of the gas, as well as that of the residual hydrogen, was read. There were 16.43 c.c. of gas; the residual hydrogen measured 1.01 c.c. at normal temperature and pressure, and thus amounted to 6.18 per cent. of the total. The volume of this gas was increased by lowering the pressure so that it was in contact with the fused potash. It was left for more than an hour; the potash, of course, was wet with the water formed by the explosion.

The capillary tubes above the stop-cock of the gas-burette, which had been twice washed out with oxygen, were pumped as empty as possible, until the vacuum-tube showed only the yellow and green lines of the mercury spectrum, and the faintest trace of a hydrogen spectrum. A strong current was passed between the electrodes so as to heat them and expel occluded oxygen. After this process had been repeated as long as was thought safe, until, as remarked, the hydrogen spectrum was extremely faint, the tap to the pump was closed. The hydrogen containing the emanation was then admitted from the explosion-burette; it was dried by passage through the narrow tube B filled with phosphoric anhydride, and it entered the bulb C, and the vacuum-tube D. This vacuum-tube was made of lead glass, with electrodes of aluminium. It was 2.5 cm. long, with a capillary of about 1 cm. in length. The aluminium electrodes were closely surrounded with glass, fused round them, so as to limit the capacity of the tube as much as possible; it was probably under one-twentieth of a cubic centimetre.

Liquid air was next poured into the jacket surrounding the bulb C, and the reservoir was raised and lowered half a dozen times, so as to convey all the gas into contact with the cooled bulb. The mercury was then raised to the level *a*, and the tap to the pump opened; and while the jacket was kept replenished with liquid air the hydrogen was pumped off, until its spectrum had almost entirely disappeared, the red line being hardly visible. The tap to the pump was then closed, the level of the mercury was raised to *b*, and the liquid air allowed to evaporate. The bulb was so bright that it was easy to read the time on a watch. The mercury was then raised to the level *c*, and the current passed. The spectrum was very brilliant, consisting of very bright lines, the spaces between them being perfectly dark; it had a striking resemblance in general character to the spectra of the gases of the argon group.

A direct-vision spectroscope, made to special design by Heele, with an illuminated scale for reading, had immediately before been standardised by noting the position of the leading lines of helium and

hydrogen. They were found to lie exactly on a scale which had previously been constructed. The new lines were read as rapidly as possible, an operation which required about half a minute. During a second reading many of the lines had faded, and the secondary spectrum of hydrogen began to appear, and rapidly grew stronger. It was identified by throwing into a field a hydrogen spectrum through the small prism; and it soon became so powerful as to mask the spectrum of the emanation completely. In order to attempt to recover it, the mercury was again drawn down to *a*, and liquid air again poured into the jacket; the emanation again condensed, and the tap to the pump was opened, and the hydrogen removed by the pump until its spectrum was again hardly visible. On repeating the series of operations already described, the spectrum of the emanation was seen a second time, but it was so transient that only the position of some of the lines could be confirmed.

Next day, only the spectrum of hydrogen was visible; its secondary spectrum was strong. The day after, the same was the case: but interposing a jar and spark-gap brought out two lines which had previously been mapped; they were very feeble.

In the table which follows, all the strong lines which were read are given; the degree of coincidence of those which are of known wave-length shows the approach to accuracy obtained; the error is probably less than five Ångström units.

| Wave-length. | Remarks.  |
|--------------|---|
| 6567         | Hydrogen C; true wave-length, 6563; observed each time.   |
| 6307         | Observed only at first; evanescent.   |
| 5975         | " " "   |
| 5955         | " " "   |
| 5805         | Observed each time; persistent.   |
| 5790         | Mercury; true wave-length, 5790.  |
| 5768         | " " " 5769.   |
| 5725         | Observed only at first; evanescent.   |
| 5595         | Observed each time; persistent and strong.  |
| 5465         | Mercury; true wave-length, 5461.  |
| 5105         | Not observed at first; appeared after some seconds; persisted, and was visible during the second examination. |
| 4985         | Observed each time; persistent and strong.  |
| 4865         | Hydrogen F; true wave-length, 4861.   |
| 4690         | Observed only at first.   |
| 4650         | Not observed when the emanation was examined again.   |
| 4630         | Ditto.  |
| 4360         | Mercury; true wave-length, 4359.  |

When the spectrum was examined two days later, besides the hydrogen and mercury lines, there were seen:—5595, feeble; 5105, feeble; 4985, very feeble; this was with a jar and spark-gap interposed; the ordinary discharge showed only the primary and secondary spectra of hydrogen, and that of mercury.

Eleven days later, the emanation from the same stock of radium bromide was collected, and treated in exactly the same manner. This time, however, an excess of conscientiousness made us continue to extract gas with the pump from the bulb C containing the frozen emanation, surrounded by liquid air, for too long a time. Every two or three strokes of the pump collected a minute bubble, occupying about the tenth of a millimetre in length of the very narrow fall-tube of the pump, which was really a fine-bore capillary. The yield of gas appeared to be continuous; and when these bubbles were examined in the dark they were brilliantly luminous. This gas was really the emanation, which possesses a feeble vapour pressure even at the temperature of liquid air. Needless to say, on attempting to examine the spectrum, little was seen, for the pressure of gas in the vacuum-tube was too low.

The tube was therefore washed out with the gas which had been pumped off, and the process was repeated. The minute bubbles which passed down the capillary fall-tube of the pump were examined, and pumping was stopped when they showed a very faint luminosity in the dark. On compressing the emanation into the spectrum-tube, the spectrum was again brilliant, and measurements were made. It was found possible to read the lines several times, for although the spectrum faded in less than a minute, it appeared to recover on ceasing to pass the current. But this recovery soon failed and, as before, nothing could be detected after 5 minutes but the primary and secondary spectra of hydrogen. Now the tube was practically vacuous before warming the bulb containing the emanation; no current would pass; but it is, of course, possible that the gas carrying the emanation had not been perfectly dried in passing through the tube B, containing phosphoric anhydride; any water-vapour would have condensed in the cooled bulb C, and would only slowly have vaporised into the vacuum-tube. On arriving there, it would give the hydrogen spectrum. Another possibility is that it may have come out of the electrodes; for it has been frequently noticed in glowing out a vacuum-tube with aluminium electrodes that even after all trace of hydrogen has been removed by passing the discharge so as to heat the electrodes, and by pumping, the hydrogen spectrum has reappeared on admitting a trace of one of the gases of the argon group, and passing the discharge for a longer time; but the intensity of the spectrum which replaced that of the emanation may perhaps warrant the supposition that hydrogen as well as helium is one of the products

of the disintegration of the emanation. This, however, is very doubtful, and judgment must be suspended until more satisfactory evidence is forthcoming.

The lines read were :—

| Wave-length. | Remarks.   |
|--------------|--|
| 6350         | Not observed before ; faint.   |
| 5975         | Observed before ; faint.   |
| 5955         | " "  |
| 5890         | Not observed before ; faint.   |
| 5854         | " " "  |
| 5725         | Observed before ; fairly strong.   |
| 5686         | Not observed before ; faint.   |
| 5595         | Observed before ; strong and persistent.                                       |
| 5580         | Not observed before ; faint.   |
| 5430         | " " "  |
| 5393         | " " "  |
| 5105         | Bright ; persistent ; observed before.   |
| 4985         | " " " "  |
| 4966         | Not observed before ; bright, but transitory.                                  |
| 4640         | Transitory ; possibly 4650 and 4630, which were seen before as distinct lines. |

The line 4966 was particularly brilliant at first ; but it soon assumed secondary importance. Some lines which had previously been observed were not seen ; they are 6307, 5805, 5137, and 4690. An attempt was made to obtain the spectrum with a jar and spark-gap ; but only hydrogen and mercury were to be seen. The resistance soon became very high, and there was danger of piercing the vacuum-tube.

Previous attempts in conjunction with Mr. Soddy gave lines with wave-length 5725 (jar), 5595 (no jar), 5105 (no jar), 4985 (no jar) ; the line 5585 was observed three times, and 5105 twice previously. The lines 6145 and 5675 mentioned in our last paper (April, 1904) were not seen, unless the latter is identical with 5580. It may perhaps be mentioned that the line 5595 was seen by Pickering in the spectrum of lightning, and was not identified with a line in the spectrum of any known gas ; it is said to have been a very strong line, of intensity 30.\*

There can be no doubt that the lines given are the chief lines in the visible spectrum of the emanation ; as for the pressure, the volume of emanation was about  $1/30,000$ th of a cubic centimetre, and the capacity of the vacuum-tube, say,  $1/20$ th ; this would make the pressure about  $1/10$ th of a millimetre. It may have been twice as much, for the numbers given are merely estimates.

It may be remembered that, at the Chemical Congress held in Paris

\* 'Astrophysical Journal,' 1901, vol. 14, p. 368.

in 1900, it was suggested that no element should receive a name until its spectrum had been mapped. Of course, the converse does not follow, that, after the spectrum of an element has been mapped, it should receive a name. The "emanation from radium," however, is a cumbrous expression, and sufficient evidence has now been accumulated that it is an element, accepting that word in the usual sense. It is true that it is only a transient element, and ought in justice to be called a compound; but of what? It stands on a wholly different plane to any known compound in the amount of heat with which it parts during its spontaneous change, and in the peculiar electrical phenomena which accompany its transformation. It is a gas; it follows Boyle's law; as Rutherford and Soddy have shown, it resembles the gases of the argon series in its indifference to chemical reagents, for it not merely withstands the prolonged action of magnesium-lime at a red heat, but also, as Ramsay and Soddy have proved, prolonged sparking with oxygen in presence of caustic potash. Its molecular weight has been found to be nearly 200, and, if it is monatomic, that number would also express its approximate atomic weight. Now, it appears advisable to devise a name which should recall its source, and, at the same time, by its termination, express the radical difference which undoubtedly exists between it and other elements. As it is derived from radium, why not name it simply "exradio"? Should it be found that the emanation, which is supposed to be evolved from thorium, is really due to that element, and not to some other element mixed with thorium in exceedingly small amount, a similar name could be given, namely, "exthorio." If the existence of actinium as a definite element is established, its emanation would appropriately be named "exactinio." It is unlikely that others will be discovered, but, if they are, the same principle of nomenclature might be applied.

It should be stated, in conclusion, that Mr. Soddy collaborated in the experiments preliminary to this successful mapping of the spectrum; had he not been obliged to leave England, he would, no doubt, have shared whatever credit may attach to this work.